Selective dehydration of methanol to dimethyl ether on ZSM-5 nanocrystals

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ABSTRACT

The effects of crystal size and mesoporosity on the performance of various synthesized ZSM-5 zeolites in catalytic dehydration of methanol to dimethyl ether (DME) reaction have been investigated. The reactions were carried out in a continuous flow fixed-bed reactor at temperatures between 180 and 320 °C and 1.1 bar. It was found that methanol conversion enhances by decreasing crystal size and increasing the reaction temperature. Uniform nanocrystal catalysts showed highest activity and stability for methanol dehydration to dimethyl ether in the temperature range studied. On the other hand, both the activity and selectivity of large crystals were low. The high activity and DME yield for the nanocrystals is due to smaller mass transport resistance for the Nano-ZSM-5 sample, due to the small crystal size. Furthermore, it was found that the selective dehydration of methanol to dimethyl ether on ZSM-5 catalyst is based on the product selectivity inside the pore channels; in other words, the selectivity to dimethyl ether should be 100% if there is no acid site on the external surface. From this evidence, it is concluded that in methanol dehydration to DME, the reaction activity is related to the crystal size, whereas the DME selectivity is determined by the uniformity of Al distribution, which determines acidity of external surface and low mass transport resistance of small crystal size. Therefore, a decrease in the number of acid sites on the external surface and reduction in crystal size are key ways to enhance catalytic selectivity and activity, respectively.

1. Introduction

Dimethyl ether (DME) is recognized as a new synthetic fuel commodity, as well as a momentous chemical intermediate. Dimethyl ether (DME), with the simple chemical formula of CH_3-O-CH_3, is a potential alternative of the energy and fuels in the future [1]. DME is commonly used as a propellant, coolant and an alternative clean fuel for diesel due to its high cetane index (*ca.* 55–60), producing no soot, no black smoke or SO_x, and the low emission of CO, NO_x and an excellent source for obtaining H_2 by catalytic steam reforming [2–5]. It can be also used as substitute for liquefied petroleum gas (LPG) that is widely used as fuel in household and industry now. DME is also a key intermediate and has been considered as an attractive alternative for producing olefins, alkyl-aromatics and other hydrocarbons from alternative source to biomass [6,7]. Therefore, DME is now attracting a considerable interest as a multi-purpose fuel for transportation, power generation and heating. In general, DME can be produced by methanol dehydration over solid porous catalysts such as zeolite, γ-Al_2O_3 [8]. Coupled with existing technologies to convert biomass to methanol, we successfully synthesized biomethanol for the first time from synthesis gas

generated by black liquor gasification [9]. In this process, black liquor is steam reformed to make syngas (hydrogen and carbon monoxide) which further is being used to produce biomethanol; some of which can be used in the conversion of methanol to dimethyl ether (DME), formaldehyde, acetic acid, land field petroleum gas (LPG), light olefins (*i.e.*, ethylene, propylene) and gasoline boiling point-range hydrocarbons [10,11]. Hence, a novel route to bio-dimethyl ether (Bio-DME) from renewable resources can be achieved.

In recent studies [1–8], the catalytic activity of ZSM-5 was tested in methanol dehydration. Despite many advantages associated with ZSM-5 such as lower cost and easy separation (from products), however, it was found that this catalyst produces undesired side products including hydrocarbons and coke, causing catalyst deactivation and ultimately stopping the process of dehydration. Therefore, researchers are trying to modify the catalyst structure and process conditions in order to optimize the DME production and improve the catalyst stability [10,12]. According to the open literature, the formation of coke on the catalyst surface was observed in the many acid catalysts [6,8,13] which inhibits the catalytic activity by leading to a decrease in DME yield during long-term operation. Recent studies have shown that one of the main reasons for catalyst deactivation (*i.e.*, coke deposition) is due to the limited size of the pores on the surface of catalyst [14,15]. In other words, enhance mass transfer in ZSM-5 zeolite either *via* reducing the size

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Table 1
Catalyst physical and chemical properties.

Catalyst	Crystal size[a] (μm)	S_{BET}[b] (m^2 g^{-1})	$S_{External}$[c] (m^2 g^{-1})	Al/(Si + Al) (mol%)		AS/AC ratio	Number of acid sites (mmol NH$_3$/g)[f]			
				In crystal[d] (AC)	On surface[e] (AS)		Weak	Moderate	Strong	Total
Nano-ZSM-5	0.12	379	113	3.48	3.58	1.03	–	–	27.00	27
Meso-ZSM-5	0.30	370	138	3.45	3.76	1.09	–	0.10	0.18	28
Con-ZSM-5	1.20	348	102	3.34	4.01	1.20	0.08	0.10	0.07	25

[a] Average particle size are estimated from SEM image.
[b] Surface areas were obtained by the BET method using adsorption data in p/p_0 range from 0.05 to 0.25.
[c] External surface area were measured by the t-plot method.
[d] Determined by ICP-AES.
[e] Determined by XPS.
[f] Obtained by the NH$_3$-TPD.

of crystals or introducing mesopores into zeolite are desirable for methanol dehydration. However, the role of ZSM-5 crystal size in methanol to dimethyl ether process has not been studied yet.

For conversion of methanol to DME, ZSM-5 is currently the most important zeolite catalyst; therefore, understanding the influence of its porosity (meso- in addition to micro-), crystal size and morphology on catalytic performance constitute a rather important topic for catalysis and reaction engineering. For operating in industrial scale application, combination of these parameters becomes an important consideration. We have previously reported the preparation of mesoporous and uniform ZSM-5 zeolites and their evaluation in catalytic conversion of methanol to hydrocarbon [7,10,11]. It was shown that decreasing crystal size increases the diffusion as expected, and that uniform ZSM-5 crystals were more effective than other crystals.

In the present work, the physicochemical and acidic properties of ZSM-5 zeolites synthesized by different methods were compared and the influence of crystal size, mesoporosity and acid site distribution on the catalytic performance in selective methanol conversion to dimethyl ether was investigated, which would be very interesting for the catalysis research community working on this field. Furthermore, the impact of reaction temperature on methanol conversion and DME selectivity is discussed.

2. Experimental

2.1. Catalyst preparation

All zeolite samples (Nano-ZSM-5, Meso-ZSM-5 and Con-ZSM-5) were prepared from clear synthesis mixtures similarly to the procedure reported in our previous studies [7,10,11] and are omitted here for brevity. All samples were treated three times in a 10 wt.% NH$_4$NO$_3$ solution at 100 °C for 1 h, rinsed and then calcined in air at 500 °C for 16 h, prior to catalytic experiments.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded using a Siemens model D 5000 diffractometer operating in Bragg–Brentano geometry. Adsorption/desorption isotherms were recorded using a Micromeritics ASAP 2010 instrument with nitrogen as adsorptive at −196 °C, and the surface area, mesopore size distribution and external surface area were calculated according to Brunauer–Emmett–Teller (BET) equation, Barrett–Joyner–Halenda (BJH) method and t-plot method, respectively. Crystal size and the shape, surface analyses of zeolites were observed using a FEI Magellan^{TM} 400L instrument and X-ray photoelectron spectra (PHI 5800) ESCA System, respectively. The average crystal length was determined by measuring the length of 50 crystals for each sample. The acidic properties were measured by temperature-programed desorption of ammonia (NH$_3$-TPD) using ThermoFinnigan TPD/R/O 1100 Series instrument. Elemental analyses (ICP-AES) were

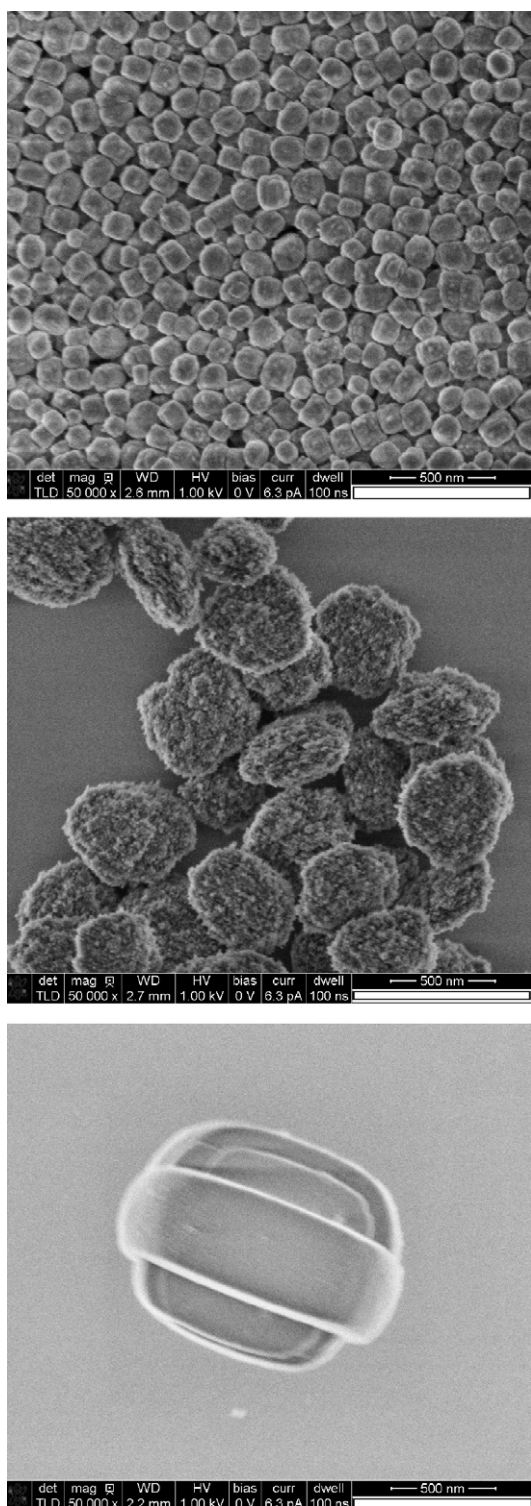carried out using a Perkin-Elmer Emission spectroscopy Model Plasma 1000.

2.3. Catalysis experiments

A flow of nitrogen saturated with methanol at 30 °C was fed to a fixed-bed reactor operating at 1.1 bar. The flow rate of nitrogen was controlled using a mass flow controller (MFC). The reactor contained 0.50 g catalyst and the temperature of the reactor was varied between 180 and 320 °C. The weight hourly space velocity (WHSV) was kept constant at 2.6 g g^{-1} h^{-1}. For each test, the ZSM-5 catalyst was sieved to 250–300 μm and diluted with inert quartz sand, then loaded to the reactor. The catalysts were loaded in a tubular reactor with an internal diameter of 17 mm and a total length of 250 mm. A thermocouple was positioned in the center of the catalyst bed in order to monitor the temperature. The catalyst was then calcined *in situ* using a heating rate of 5 °C/min under a flow of synthetic air (30 mL/min). When the reactor temperature reached 500 °C, it was maintained for 4 h. The temperature was then decreased to the reaction temperature in flowing air. To avoid possible condensation of hydrocarbons, the temperature of the effluent line was constantly maintained at 100 °C. The products were analyzed on-line by Gas Chromatography using a Varian 3800 equipped with a flame ionization detector (GC-FID) and a capillary column (CP-Sil PONA CB fused silica WCOT) to separate methanol, DME, and C$_1$–C$_{10}$ hydrocarbons. Helium was used as a carrier gas. The first sampling of the product gas was done 1 h after the feed was introduced to the reactor.

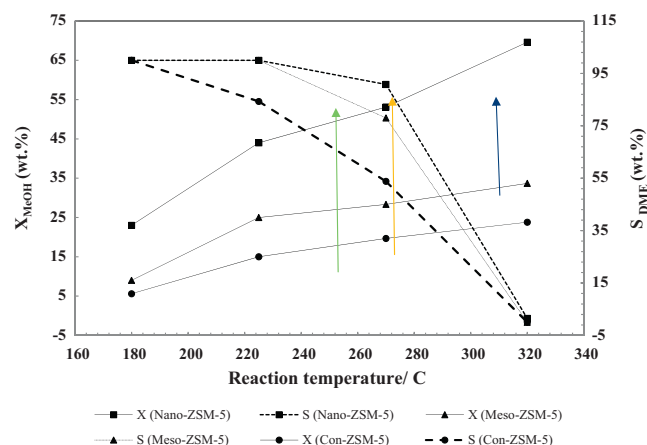## 3. Results and discussion, catalytic performance measurements

3.1. Catalyst characterization

All zeolite samples showed similar X-ray diffraction patterns (not shown), typical of ZSM-5 and no other phases than ZSM-5 were identified. SEM images of Nano-ZSM-5, Meso-ZSM-5 and Con-ZSM-5 are shown in Fig. 1a–c, respectively. For each catalyst, the length of approximately 50 crystals was measured and average values are listed in Table 1. The nano-ZSM-5 sample is comprised of very small pseudo-cubic crystals with an average length of about 0.11 μm. The meso-ZSM-5 crystals display a more rounded habit and the average length is about 0.30 μm. On the other hand, the crystals in the con-ZSM-5 sample displayed the typical habit of twinned ZSM-5 crystals with a length of about 1.3 μm in the *c*-direction. As shown in Table 1, the BET surface areas of all zeolites samples are similar and between about 350–380 m^2 g^{-1}. All zeolite samples also display similar external surface areas, about 100–140 m^2 g^{-1}, which indicates a similar and significant amount of mesopores in all samples. The quantitative estimation of acid sites (the amount of adsorbed ammonia), which obtained by the NH$_3$-TPD are summarized in Table 1. From the results presented in Table 1, it can

Fig. 1. SEM images of ZSM-5 crystals synthesized by different methods (a) uniform ZSM-5 single crystal (Nano-ZSM-5), (b) mesoporous ZSM-5 crystal (Meso-ZSM-5), and (c) conventional ZSM-5 crystal (Con-ZSM-5). The same batch of reaction solution mixture was used for both experiments.

Fig. 2. Change in conversion of methanol and selectivity to DME with reaction temperature on H-ZSM-5 catalysts. Reactant, methanol; WHSV, 2.6 g g^{-1} h; time on stream, 15 h; pressure, 1.1 bar.

usually ascribed to NH_3 desorption from moderate and strong acid sites. On the other hand, the Con-ZSM-5 catalyst contains three desorption peaks at 245 °C, 265 °C and 420 °C that correspond to weak, moderate and strong acid sites, respectively. Results of elemental analysis (ICP-AES) showed that all zeolite catalysts contained about the same amount of aluminum (AC), about 3.3–3.5 mol%, that roughly corresponds to the amount of Si and Al in the initial synthesis mixture for hydrothermal synthesis. From the results of XPS, the surface Al content (AS) was calculated. The AS/AC ratios indicate that more Al concentrated on the external surface of Con-ZSM-5 than on those of Nano-ZSM-5 and Meso-ZSM-5. Ballmoos and Meier [16] have already been pointed out the surface concentration of Al in a large crystal of ZSM-5. The inhomogeneous distribution of Al in ZSM-5 crystals can be prevented by the constant stirring applied during the hydrothermal synthesis. To summarize, the characterization of the three zeolite catalysts shows that the samples are quite similar, with only one major difference, *i.e.*, the crystal size.

3.2. Effect of crystal size on catalytic activity in methanol conversion and DME selectivity

In this research, the catalytic performance of ZSM-5 catalysts with different size and shape, namely, Nano-ZSM-5, Meso-ZSM-5 and Con-ZSM-5 were investigated in selective dehydration of methanol to dimethyl ether at various reaction temperatures. The change in the conversion of methanol as a function of reaction temperature is shown in Fig. 2. On all catalysts, the conversion of methanol enhanced with the increase in reaction temperature. However, the conversion of methanol on Nano-ZSM-5 was slightly and significantly higher than those on Meso-ZSM-5 and Con-ZSM-5, respectively. The order of conversion of methanol is Nano-ZSM-5 > Meso-ZSM-5 > >Con-ZSM-5, which is the same order as surface area and the reverse order of crystal size.

In our previous investigations [7,10,11], we found that methanol conversion increased either by the scaling down of zeolite crystals to form a nanometer scale; or, by introducing mesopore into ZSM-5 crystals. Small and mesoporous ZSM-5 crystals with a higher external surface area offer more pore entrances than large (microsize) crystals. The conversion of methanol on Nano-ZSM-5 and Meso-ZSM-5, having a small crystal size and higher mesoporosity is easier to occur inside pore channels than on the large crystal size, as well as less mesoporosity, *i.e.*, Con-ZSM-5. This result indicates strongly that the uniform nanocrystal size of ZSM-5 is necessary for effective conversion of methanol. The higher conversion on uniform ZSM-5 nanocrystals and mesoporous ZSM-5 crystals than on large ones

be observed that, for all zeolites, the estimated total density values were almost similar, *i.e.*, 0.27, 0.28, and 0.25 mmol/g for Nano-ZSM-5, Meso-ZSM-5, and Con-ZSM-5 zeolites, respectively. As resulted, Nano-ZSM-5 catalyst has a peak at about 450 °C which corresponds to strong acid sites. In the case of Meso-ZSM-5, two distinct desorption peaks were observed at ~275 and 460 °C in NH_3-TPD, which are

Table 2
Methanol conversion; DME selectivity and yield as a function of crystal size, surface acidity and reaction temperature.

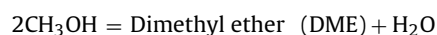| Catalyst	Crystal size[a] (μm)	Reaction temperature[b] ($^\circ$C)	X_{MeOH}[c] (wt.%)	Selectivity (wt.%)[d]		Y_{DME}[e] (wt.%)
				DME	HCs	
Nano-ZSM-5	0.12	180	23.0	100	–	23
		225	44.0	100	–	44
		270	53.1	90.8	9.2	48
		320	69.6	1.5	99.0	1
Meso-ZSM-5	0.30	180	16.0	100	–	16
		225	40.0	100	–	40
		270	45.0	78.0	22.0	35
		320	53.0	–	100	–
Con-ZSM-5	1.20	180	10.9	100	–	11
		225	25.0	84.3	16.0	21
		270	32.0	53.8	46.0	17
		320	38.2	–	100	–

[a] Average particle size are estimated from SEM image.
[b] Methanol dehydration reaction temperature ($^\circ$C).
[c] Average of methanol conversion; time on stream = 15 h; 1.1 bar; WHSV = 2.6 g g^{-1} h.
[d] Average of DME selectivity; time on stream = 15 h; 1.1 bar; WHSV = 2.6 g g^{-1} h.
[e] Average of DME yield; time on stream = 15 h; 1.1 bar; WHSV = 2.6 g g^{-1} h.

should be explained by the fact that more pore entrances are available on the nanocrystal surface. Because the intercrystalline spaces in nanocrystals are directly accessible from the outer surface of the ZSM-5 and the intercrystal diffusions of reactants and products to/from active site located in micropore are much higher than those inside large microsize ones. In these cases, the condition that mesopores enhance the mass transport to/from the active sites in the zeolite materials has been satisfied [17]. Therefore, it is concluded that by reducing crystal size and increasing external surface area in ZSM-5 nanocrystals both increase accessibility to acid sites and enhances the diffusion rate of reactants and products; consequently, catalytic stability and conversion rate can be improved accordingly. In fact, such findings are promising in developing stable catalysts for methanol dehydration reaction.
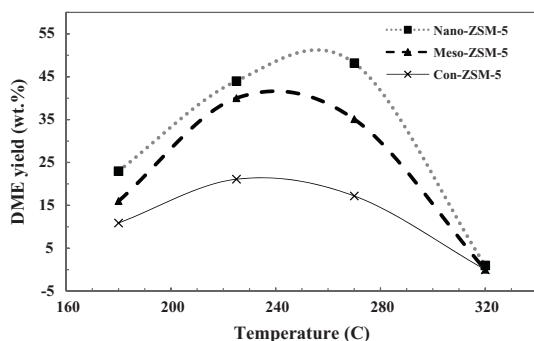
The DME selectivity obtained over all the ZSM-5 catalysts are compared in Fig. 2. It follows from this figure that DME selectivity of catalysts changed with reaction temperature, mainly due to the change in methanol conversion with temperature. The influences of crystal size, external surface area, acid sites and reaction temperature on products distribution (i.e., selectivity to DME and hydrocarbons, also yield of DME) are summarized in Tables 1 and 2. It follows from Fig. 2 and Table 2 that higher reaction temperature resulted in increased methanol conversion and decreased yield of DME. As shown in Fig. 2, the selectivity to DME decreased with increasing reaction temperature from 270 to 320 $^\circ$C. On the contrary, other hydrocarbons (C$_1$–C$_{10}$) selectivity increased from 9.2% to 98.5% with increasing reaction temperature from 270 to 320 $^\circ$C. Similar changes in selectivity with conversion were observed for both crystals. Although the difference in SiO$_2$/Al$_2$O$_3$ ratios of all catalysts was not very large (Table 1), the reactions of methanol with catalysts surfaces were certainly different, thus leading to different conversions and products distributions (Table 2). The reaction temperature, crystal size and acid sites distributions influence the dehydration reaction of the catalysts affecting all products coming from micro/mesopores. This can explain why a higher yield of DME was achieved with Nano-ZSM-5. The results clearly indicate that the relative dehydration rate and products distributions of methanol over various ZSM-5 crystals are functions of external surface area, the number of strong acid sites, crystal size and reaction temperature. According to the criteria reported above, we conclude that crystal size, mass transfer of reactants and products and reaction temperature significantly affect the methanol dehydration rate. The main product was DME by dehydration of methanol at any temperature except 320 $^\circ$C. Other hydrocarbons were produced

on any catalyst at 320 $^\circ$C. It is known that methanol conversion to hydrocarbons is a series of reaction by which methanol is first dehydrated to dimethyl ether (DME) and water and then DME is converted to light olefins [8,10,18,19]. The mechanism of DME, light olefins, paraffins and alkyl aromatics formation from methanol is presented as:

$$2CH_3OH = \text{Dimethyl ether } (DME) + H_2O$$
$$\rightarrow \text{light olefins } (\text{ethylene \& propylene}) + H_2O$$
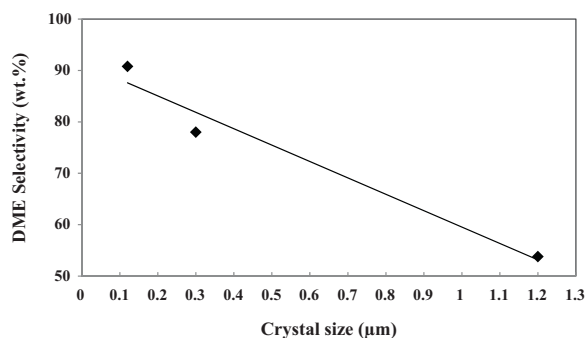$$\rightarrow \text{iso-and cyclo-paraffins, alkyl aromatics}$$

According to the order of Nano-ZSM-5, Meso-ZSM-5 and Con-ZSM-5, the percentage of DME decreased while that of hydrocarbons increased. Furthermore, on Nano-ZSM-5 and Meso-ZSM-5 the DME selectivity showed almost no change with the variation of temperature from 180 to 225 $^\circ$C. At 270 $^\circ$C, the methanol conversion and DME selectivity on Meso-ZSM-5 were slightly and significantly lower respectively, compared with Nano-ZSM-5. Both catalysts gave 100% selectivity of other hydrocarbons at 320 $^\circ$C. On the contrary, the DME selectivity on Con-ZSM-5 varied with reaction temperature significantly; or, the percentages of DME decreased while that of other hydrocarbons increased with the increase in reaction temperature. It is confirmed that nanocrystals are also necessary to DME selectivity inside the pore channels of ZSM-5, preventing by further dehydration reaction of DME to other hydrocarbons.

The change in the yield of DME at various temperatures is shown in Fig. 3 and listed in Table 2. The yield of DME on Nano-ZSM-5 was slightly and significantly higher than those on Meso-ZSM-5 and Con-ZSM-5, respectively. Furthermore, the order of yield of DME is the reverse order of crystal size. The maximum yield to DME was about 48% on Nano-ZSM-5 at 270 $^\circ$C. The correlation between selectivity to DME and the crystal size and AS/AC (see Table 1) ratio at 270 $^\circ$C is plotted in Figs. 4 and 5, respectively. This graph showed that the selectivity to DME is inversely proportional to crystal size and AS/AC ratio. Meanwhile, by extrapolation of the line in Fig. 5, it is found that the selectivity to DME should be 100% if AS/AC become one. Therefore, if there is less or even no acid site on the external surface, all of methanol could be converted to DME. This fact strongly indicates that the selective dehydration of methanol to DME on ZSM-5 crystal is the basis for the mass transport limitation inside the pore channels. Previously, Kustova et al. [19] investigated
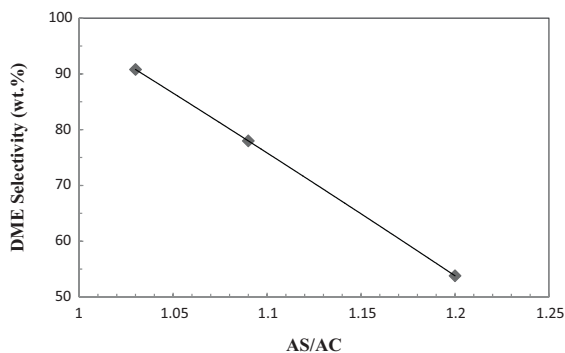
Fig. 3. DME yield with reaction temperature in methanol conversion on H-ZSM-5 catalysts. Reactant, methanol; WHSV, 2.6 g g^{-1} h; time on stream, 15 h; pressure, 1.1 bar.

Fig. 4. Correlation between selectivity to DME and the crystal size; reactant, methanol; WHSV, 2.6 g g^{-1} h; reaction temperature, 270 °C; time on stream, 15 h; pressure, 1.1 bar.

the effects of silicalite shell on the catalytic properties of ZSM-5-type materials in the methanol dehydration reaction. Core-shell ZSM-5 crystals were prepared by a certain amount of ZSM-5 crystals (cores) that was hydrothermally treated in a silicalite synthesis gel. Silicalite is an aluminum-free coated on the external surface of ZSM-5 crystals and should be catalytically inactive during the reaction. The results show that the addition of the silicalite shell to the ZSM-5 samples improves the resistance towards carbon formation in the methanol dehydration reaction.

All aforementioned catalysts with almost similar total number of acid sites (Table 1) show slightly and significantly differences in methanol conversion and the yield of DME. Here it is necessary and reasonable to compare the activities of catalysts on the basis of crystal size and acid sites density. The methanol conversion is basically proportional to surface area and density of strong acid

Fig. 5. Correlation between selectivity to DME and the AS/AC; reactant, methanol; WHSV, 2.6 g g^{-1} h; reaction temperature, 270 °C; time on stream, 15 h; pressure, 1.1 bar.

sites in catalyst. This result indicates that the acid site distribution determine the reaction selectivity, therefore, it is concluded that by reducing crystal size and also decreasing in the acid sites on the external surface are the certain ways to prove the selectivity to DME in methanol dehydration on ZSM-5 catalyst. Furthermore, on the contrary to large ZSM-5 crystal (Con-ZSM-5), nano-sized ZSM-5 crystal (Nano-ZSM-5) retards the coke formation, resulting in high catalytic stability. This can be verified in observing a significant difference in the colour of the both catalysts after 15 h reaction that may be attributed to the slower coke formation and higher diffusion rate in uniform ZSM-5 nanocrystals.

In addition, elucidating the relationship between accessibility and reactivity is of great importance for the optimization of the catalytic performance during catalytic dehydration process. Through the choice of crystal size and reaction temperature, the process can be tailored to maximize DME yield. Therefore, it is believed that the great enhancement effect the uniform Nano-ZSM-5 in methanol conversion was mainly due to the effect of smaller mass transport resistance on uniform nanocrystals. In previous investigations, it has been demonstrated that the shape selectivity is negligible due to linear and unbranched structure of methanol and DME molecules [20,21]. This study showed that in larger crystals (Con-ZSM-5), DME (as intermediate) can be readily converted in consecutive steps before it is desorbed from the crystal. Therefore, more hydrocarbon products and faster deactivation were observed when using this catalyst, due to longer intra-crystalline diffusion path lengths. Where as in smaller crystals (Nano-ZSM-5), faster equilibration of methanol and DME and highest catalyst stability can be obtained at low temperature and conversion. In additions, as the results show (see Table 1 and Fig. 2) role of surface area in increased rate of DME production (non-shape selective products) is more significant in smaller ZSM-5 crystals. This can be verified in observing a significant difference in methanol conversion of Nano-ZSM-5 catalyst at all temperatures due to the difference in diffusion rate of reactants into catalysts. Finally, it is concluded that methanol conversion and yield to DME on ZSM-5 are significantly dependent upon crystal size.

4. Conclusions

Comparison of results obtained through catalyst characterization and evaluations pointed out that the ZSM-5 with uniform nanocrystal size contained less Al on the external surface area than that prepared by the conventional method. In methanol to DME, the reaction activity is related to the crystal size, whereas the DME selectivity is determined by acid site distribution on external surface and in the bulk crystal. Selectivity to DME and catalyst stability were enhanced as the crystal size were reduced due to faster mass transfer of products from the crystals and pores, therefore reducing the formation of coke at all reaction temperatures. It was also found that uniform ZSM-5 nanocrystals are the most active and selective catalyst for methanol dehydration and DME production.

References

[1] S.P. Naik, T. Ryu, V. Bui, J.D. Miller, N.B. Drinnan, W. Zmierczk, Chem. Eng. J. 167 (2011) 362–368.
[2] G. Centi, S. Perathoner, Catal. Today 148 (2009) 191–2005.
[3] H. Herring, Energy 31 (2006) 10–20.
[4] T. Semelsberger, R. Borup, H. Greene, J. Power Sources 156 (2006) 496–511.

[5] G. Olah, A. Goeppert, G. Surya Prakash, J. Org. Chem. 74 (2009) 487–498.
[6] J. Freiding, B. Kraushaar-Czarnetzki, Appl. Catal. A: Gen. 391 (2011) 254–260.
[7] A.A. Rownaghi, F. Rezaei, J. Hedlund, Catal. Commun. 14 (2011) 37–41.
[8] M. Stöcker, Micropor. Mesopor. Mater. 29 (1999) 3–48.
[9] C. Häggström, O. Öhrman, A.A. Rownaghi, J. Hedlund, R. Gebart, Fuel Process. Technol. 94 (2012) 10–15.
[10] A.A. Rownaghi, J. Hedlund, Ind. Eng. Chem. Res. 50 (2011) 11872–11878.
[11] A.A. Rownaghi, F. Rezaei, J. Hedlund, Micropor. Mesopor. Mater. 151 (2012) 26–33.
[12] S. Hassanpou, F. Yaripou, M. Taghizadeh, Fuel Process. Technol. 91 (2010) 1212–1221.
[13] D.M. Bibby, N.B. Milestone, J.E. Patterson, L.P. Aldridge, J. Catal. 97 (1986) 493–502.
[14] G.V. Echevsky, A.B. Ayupov, E.A. Paukshtis, D.J.O. Rear, C.L. Kibby, Stud. Surf. Sci. Catal. 139 (2001) 77–84.
[15] J. Perez-Ramırez, S. Abello, A. Bonilla, J.C. Groen, Adv. Funct. Mater. 19 (2009) 164–172.
[16] R.V. Ballmoos, W.M. Meier, Nature 289 (1981) 782.
[17] M.S. Holm, E. Taarning, K. Egeblad, C.H. Christensen, Catal. Today 168 (2011) 3–16.
[18] F.J. Keil, Micropor. Mesopor. Mater. 29 (1999) 49–66.
[19] M. Kustovaa, M.S. Holma, C.H. Christensenb, Y.H. Pana, P. Beatoa, T.V.W. Janssensa, F. Joensena, J. Nerlova, Stud. Surf. Sci. Catal. 174 (2008) 117–122.
[20] N. Khandan, M. Kazemeini, M. Aghaziarati, Appl. Catal. A: Gen. 349 (2008) 6–12.
[21] J.L.G. Cimadevilla, R. Alvarez, J.J. Pis, Vib. Spectrosc. 31 (2003) 133–139.